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ULTRAVIOLET STABILITY OF SOME MODIFIED METAL PHOSPHATES

FOR THERMAL-CONTROL SURFACES

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### ABSTRACT

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The ultraviolet and thermal stabilities of chemical conversion coatings based on aluminum and chromium phosphates have been investigated. The optical properties of these coatings are useful in aerospace applications as thermal-control surfaces since their ratio of solar absorptance to thermal emittance ( $\alpha_s/\epsilon$ ) can be adjusted by using the appropriate surface thickness and/or treating the thermal-control surface with an alkali metal hydroxide. The ratio of solar absorptance to thermal emittance can be decreased from 1 to 0.5 by reacting the aluminum and chromium phosphate surface with one normal sodium hydroxide. The exposure of these surfaces at room temperatures to ultraviolet radiation in a vacuum increases the solar absorptance by about 10 to 20 percent of the original value. On the other hand, the change in the thermal emittance was found to be a function of the sample temperature during the ultraviolet exposure. When the samples were maintained near room temperature, the thermal emittance was found to decrease approximately 20 to 30 percent; however, when the sample was cooled to 0° C, the reverse was noted. In the latter case, the emittance increased sufficiently to result in an overall decrease in the ratio of  $\alpha_s/\epsilon$ .

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INTRODUCTION

As a result of an increasing number of orbital missions extending over long periods, there has been considerable need for thermal-control surfaces which are "stable" to the space environment, that is, surfaces which retain their original optical properties after extended exposure to the space environment. A considerable amount of work has recently been directed toward developing and testing such coatings (ref. 1-4). In some instances, such as the Echo passive communications satellite program, the thermal-control coatings must meet further stringent requirements. The thermal-control surface of the Echo (A-12) is approximately 57,000 square feet. The total structural shell of the Echo (A-12) is only 0.75 mil thick and is composed of two outer layers of 0.18 mil aluminum foil glued to a 0.35-mil Mylar plastic film as shown in figure 1. As a result of the very large surface and the very thin substrate, it was necessary to use a thermal-control surface with a minimum weight and thickness.

Chemical conversion coatings have proved to be the most practical approach to this problem. A mixture of chromium phosphate and aluminum phosphate deposited by a dip process on the thin outer aluminum foil was successful. This coating was a commercial product, Alodine 401-45<sup>1</sup>. It was necessary to investigate the ultraviolet stability of its optical properties over extended times since Alodine had previously been used primarily as a paint primer and weather protectant for

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<sup>1</sup>Trade mark of Amchem Products, Inc., Ambler, Pennsylvania.

aluminum, and virtually nothing was known of its use for thermal-control purposes.

#### Determination of Solar Absorptance and Thermal Emittance

The total hemispherical reflectance from 0.2 to 2.1 microns was measured with a Cary-14 spectrophotometer equipped with an integrating sphere coated with barium sulfate. Freshly smoked magnesium oxide plates were used as reflectance standards. Calculations of solar absorptance were made by determining the reflectance of the specimen for each wavelength increment corresponding to a 1-percent energy increment under the solar-energy curve. These weighted reflectance increments were then summed over the 0.295-to-2.02-micron range and the total reflectance subtracted from unity.

The "total hemispherical reflectance" from 4 to 15 microns was measured with a Perkin Elmer 13-U spectrophotometer equipped with a hohlraum attachment. The emittance values were calculated by determining the reflectance of the specimen for each wavelength increment corresponding to a 1-percent energy increment under a 295° K blackbody curve. These weighted reflectance increments were then summed over the 4-to-15-micron range (with allowance being made for the fact that this spectral region contains only 53 percent of the blackbody energy) and subtracted from unity. The resultant value is referred to in this paper as thermal emittance. Preliminary data recently obtained by a calorimetric technique indicates that the spectrophotometric method, for the phosphate coating in the 4-to-15-micron range, is systematically high in  $\epsilon$  by about 0.02.

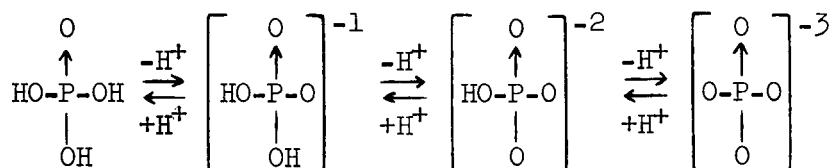
#### Chemical Conversion Coatings

The chemical conversion coating, Alodine 401-45, is produced by reacting an aluminum surface with an aqueous solution of chromic, phosphoric, and hydrofluoric

acids. Clemmons and Camp (ref. 4) have reported that the ratio of solar absorptance to thermal emittance ( $\alpha_s/\epsilon$ ) varies from 7.0 to 0.80 as a function of the surface densities, which varied from 30.4 milligrams per square foot to 426 milligrams per square foot, respectively. They also found that the solar absorptance increases initially and then remains virtually constant over a wide range of surface densities (thickness). In contrast, the thermal emittance was found to increase almost linearly over the same range of surface densities. This variation of thermal emittance with surface density permits a wide range of equilibrium temperatures for an Alodine 401-45 coated satellite simply by selecting the appropriate surface density with the desired  $\alpha_s/\epsilon$  ratio. Since the thermal emittance of this type of surface is the controlling factor in its useful optical properties, attention was focused on the infrared spectra of these coatings (ref. 5).

A typical infrared absorptance spectrum for Alodine 401-45 is shown in figure 2 along with a plot of the spectral-energy distribution for a 300° K blackbody. There are two prominent peaks in this infrared spectrum. The peak in the 3.8-micron region, which has been attributed to the acidic hydroxyl group (ref. 6), is of much less significance to the thermal emittance than the broad peak in the 7.5-to-11-micron region, which is due to the phosphate group (refs. 6 and 7). The reason is that over 25 percent of the total energy of a 300° blackbody falls within the 8- to 12-micron region whereas less than 1 percent of the total energy for a 300° K blackbody is found at wavelengths shorter than 4 microns. If the chemical nature of the phosphate group could be sufficiently changed to alter the intensity of the broad peak at 7.5 to 11 microns it would be possible to increase the thermal emittance of the Alodine 401-45 surface without resorting to an increase in surface density. Alteration of this group is possible

by varying the acidic nature of the phosphate group as shown below:



By causing the above series of equilibria to shift toward the right, the vibrations of the P-O bond should be changed. The subsequent decrease in the hydroxyl content should reduce the possibility of hydrogen bonding involving the OH group and thus permit increased P-O vibrations. Increased P-O vibrations would result in an increase in the intensity at the 7.5- to 11-micron band and hence a surface with a higher emittance.

A series of experiments were carried out to test this hypothesis. Samples of Alodine 401-45 on the Echo (A-12) laminate were reacted with dilute sodium and potassium hydroxide solutions for times ranging from 10 to 60 seconds. After washing in water and drying in air, the infrared-absorption spectra were again determined. The band at 7.5 to 11 microns was found to increase whereas the acidic OH band at 3.8 microns was found to decrease with reaction time in the basic solution, as shown in figure 3. The resultant increase in the thermal emittance was found to be linear with reaction time from an  $\epsilon$  of 0.2 to 0.4.

In addition to increasing the thermal emittance of the Alodine 401-45 surface, it was found that the solar absorptance and surface weight both decreased with reaction time as illustrated in figures 4 and 5, respectively. The overall effect of this treatment is to decrease the ratio of  $\alpha_s/\epsilon$  as shown in figure 6. This approach to modifying the surface of Alodine 401 now makes it possible to obtain lower  $\alpha_s/\epsilon$  ratios without the necessity of increasing surface densities, as previously described (ref. 4).

## Stability to Ultraviolet, Thermal, and Vacuum Environments

Exposure to ultraviolet and thermal environments are known to produce changes in the optical properties of thermal-control surfaces and coatings (refs. 1, 8, and 9). Most of the reported investigations of the stability of thermal-control surfaces have been concerned with the effects of ultraviolet radiation in a vacuum on the solar absorptance of the surfaces. In the case of thermal coatings which contain small molecular species of moderate volatility, it is reasonable to expect some effect from long-term exposure to elevated temperatures in a vacuum as well as ultraviolet effects. Very little has been reported on thermal effects alone, though in some cases the temperature of the specimen during exposure to ultraviolet can have a significant effect, even to the extent of obscuring the effects of the ultraviolet exposure.

The conditions and environments used for studying the stability of the aluminum and chromium phosphate coatings are summarized below.

### ENVIRONMENTAL CONDITIONS

Radiation	Pressure, torr	Temperature, °C
Thermal	1	100
Ultraviolet <sup>1</sup>	10 <sup>-6</sup>	70
Ultraviolet <sup>1</sup>	10 <sup>-6</sup>	0
Ultraviolet <sup>1</sup>	10 <sup>-7</sup>	25

<sup>1</sup>Intensity, approximately 3 to 4 suns. (BH-6 lamp.)

In studying the effects of ultraviolet radiation on the optical properties of thermal-control surfaces, it is essential that the specimen temperature be well known and maintained as constant as possible so as not to obscure the ultraviolet effect with thermal effects. When the ultraviolet intensity is considerably higher than solar intensity, the high thermal output of the source increases the difficulty in maintaining the desired sample temperature. A comparison of thermal

and ultraviolet effects on solar absorptance and thermal emittance is shown in figure 7. The decrease in emittance is probably due in a large part to loss of water and is nearly the same for the thermal and ultraviolet tests. There is some evidence for this as shown by the decrease in the absorbed water peak (ref. 10) at 6.1 microns in figures 8 and 9. The change in  $\alpha_s/\epsilon$  is shown in figure 10 for the thermal (100° C) and for the ultraviolet exposure at 25° and 0° C. The spread in values of  $\alpha_s/\epsilon$  for the ultraviolet exposure at 25° C are, in part, due to different initial values of  $\alpha_s/\epsilon$ .

In general, the thermal and ultraviolet tests at 100° C and 25° C, respectively, resulted in an increase in  $\alpha_s$  of 10 to 20 percent and a decrease in  $\epsilon$ . The overall effect was an increase in the  $\alpha_s/\epsilon$  ratio. The converse was found for those specimens which were maintained at 0° C during the exposure at  $10^{-6}$  torr to ultraviolet radiation from a BH-6 lamp where a large increase in  $\epsilon$  more than compensated for a slightly higher increase in  $\alpha_s$ . A comparison of the spectra of specimens after ultraviolet irradiation at different temperatures is illustrated in figures 9 and 11. The infrared spectra of the surfaces irradiated at 0° C resemble those from the sodium hydroxide treated surface with the exception that the 3.8-micron peak is increased instead of decreased. The absorbed water is apparently trapped in or on the surface at 0° C in sufficient amounts such that it is available to undergo photo-induced interactions with the mixed phosphates in the thermal-control surface. The literature is exceedingly sparse in regard to basic studies on the photolysis of metal phosphates. Additional studies are required to describe more fully the nature of this effect.

## CONCLUSIONS

1. The optical properties of chemical conversion coatings can be altered by controlled post-treatments of the surface to provide a wider range of  $\alpha_s/\epsilon$  values without increasing surface thickness.

2. Temperatures of test specimens can be as important, or more important, than the degree of vacuum or ultraviolet flux in ascertaining the stability of optical properties for thermal-control surfaces.

3. More attention should be devoted to the basic spectrophotometric techniques for determining the cause of changes in optical properties as well as development of new thermal-control surfaces.

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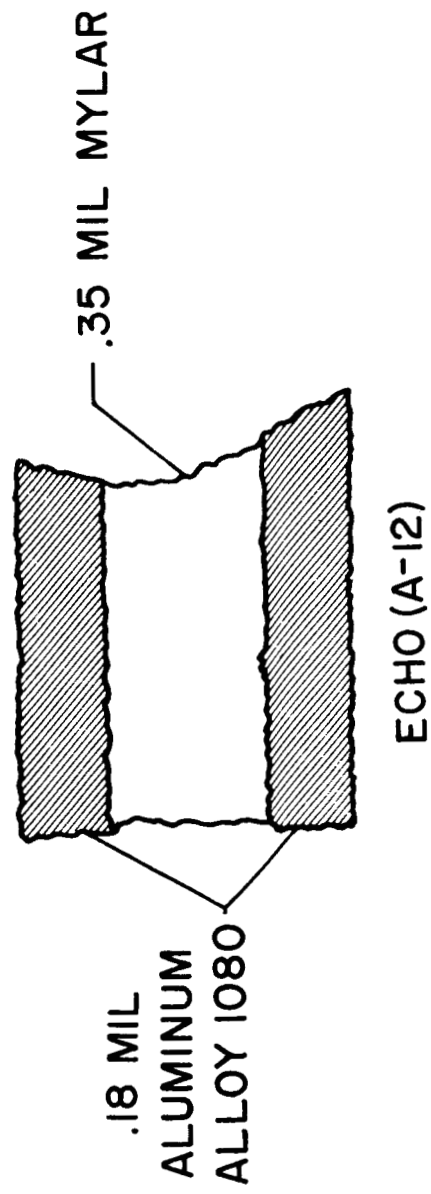


Figure 1.- Cross section of Echo A-12 laminate.

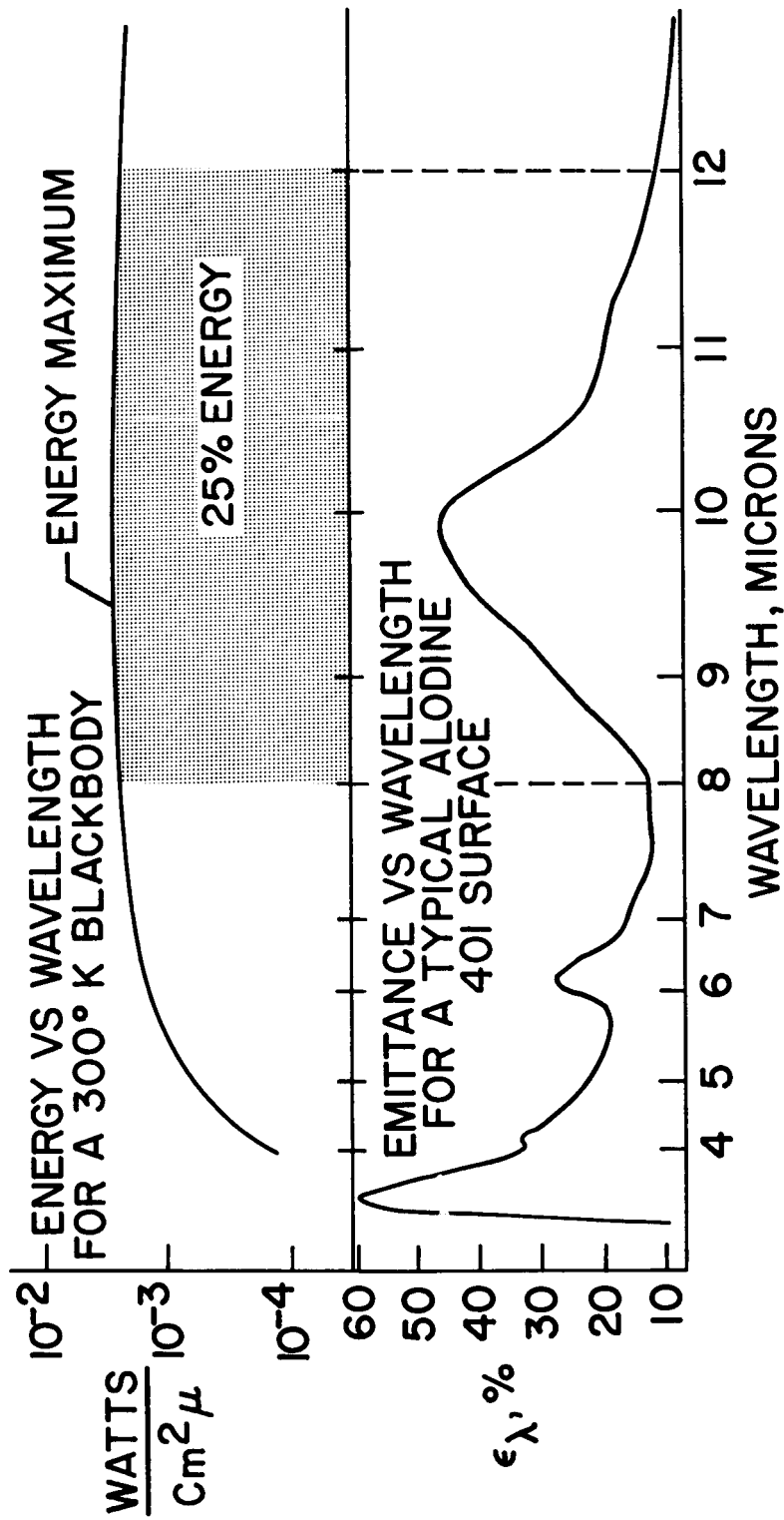
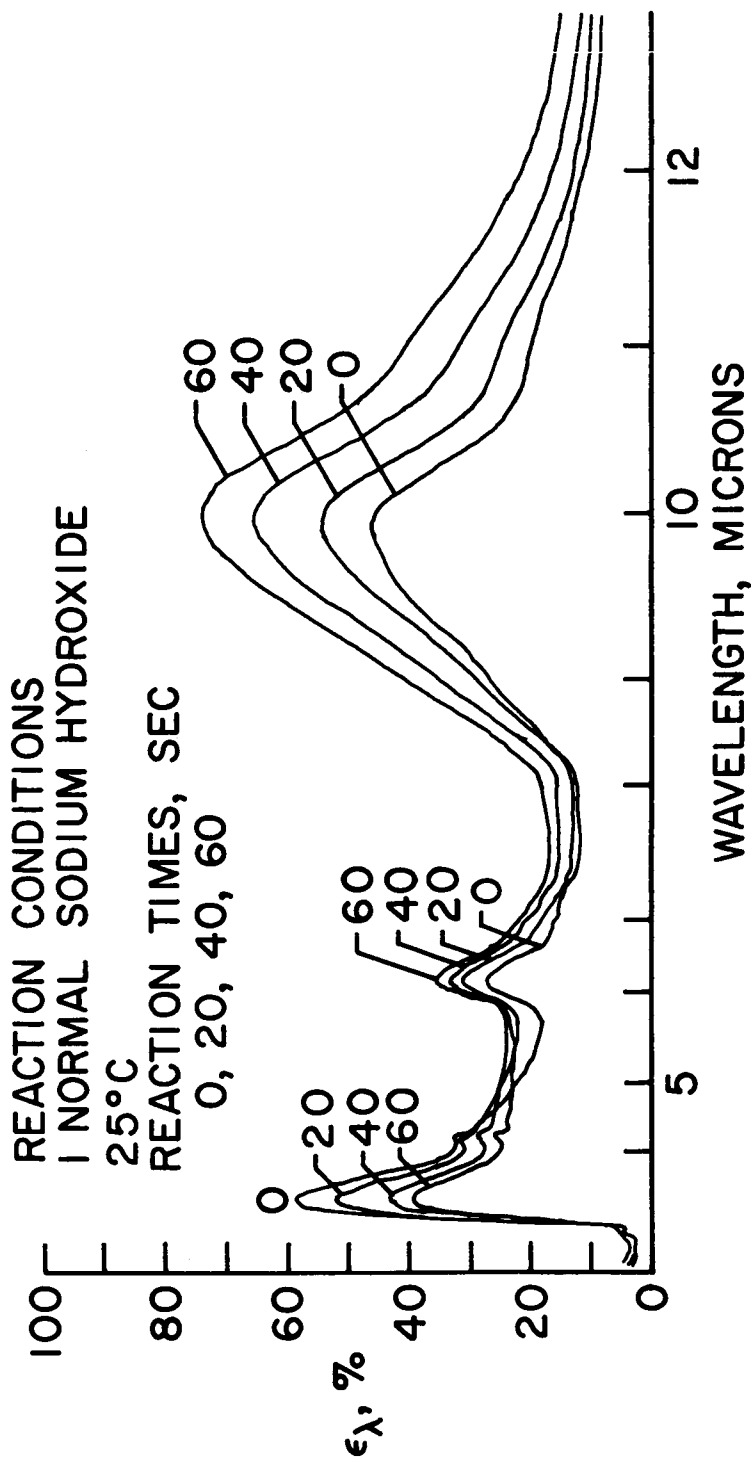
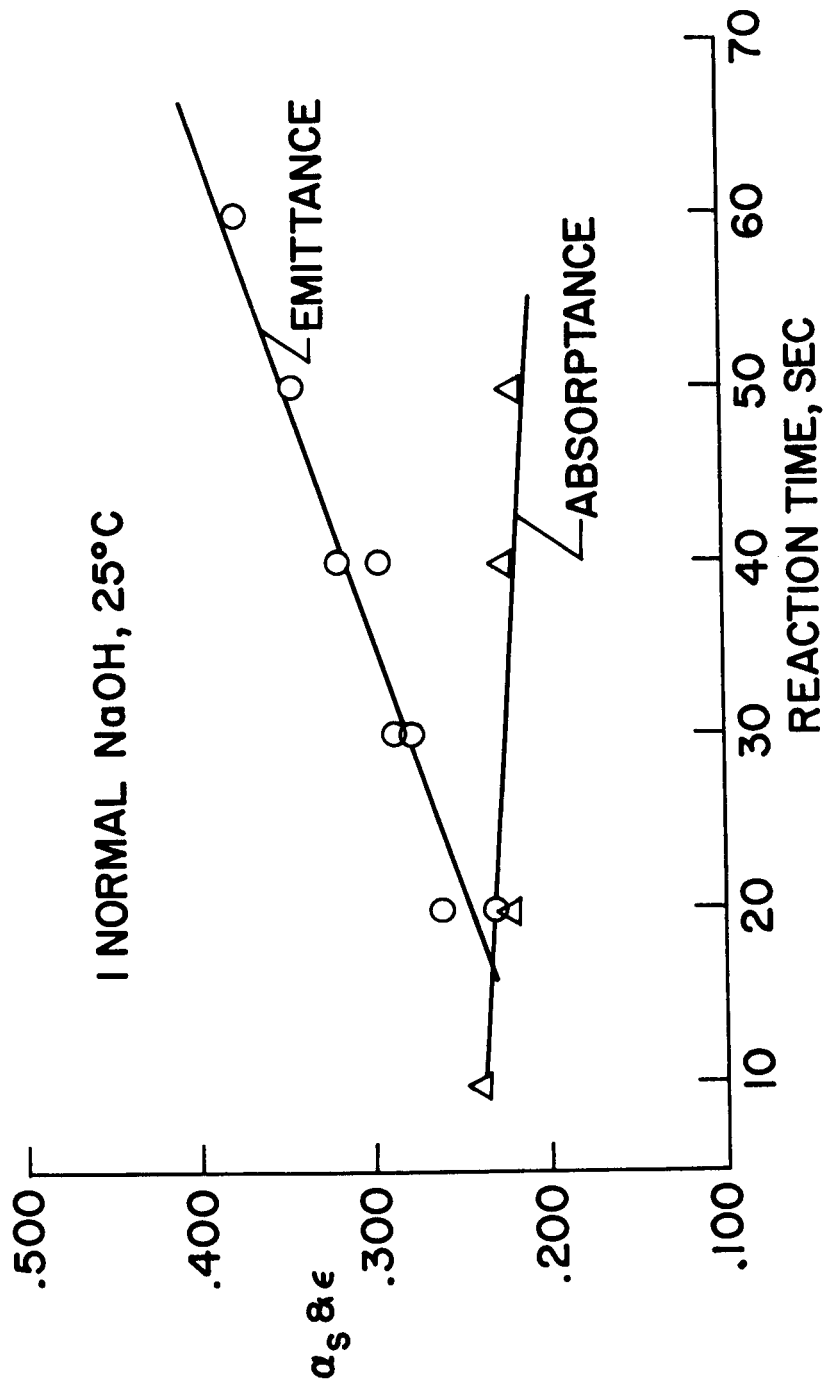


Figure 2.- Comparison of blackbody spectra with emittance spectra of Alodine 401.



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Figure 3.- Influence of hydroxide treatment on infrared spectra of Alodine 401.



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Figure 4.- Influence of hydroxide treatment on solar absorptance and thermal emittance of Alodine 401.

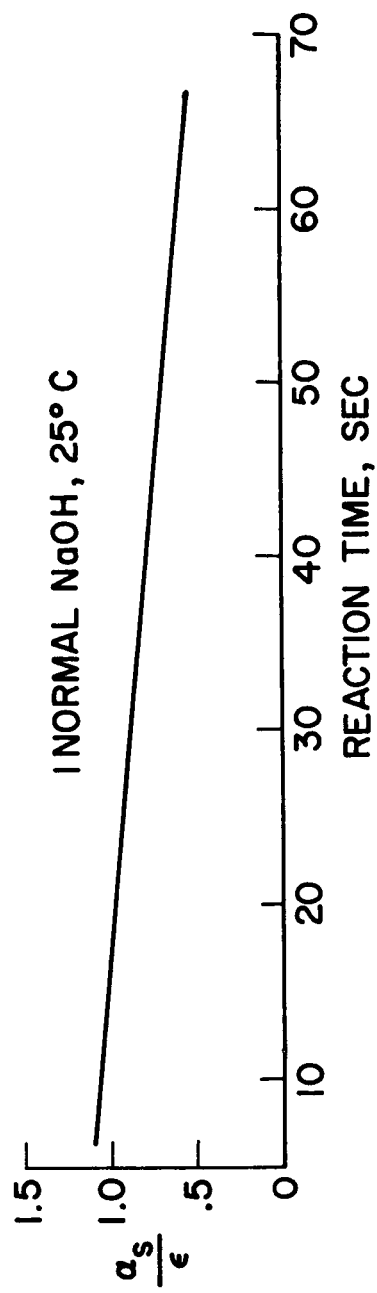
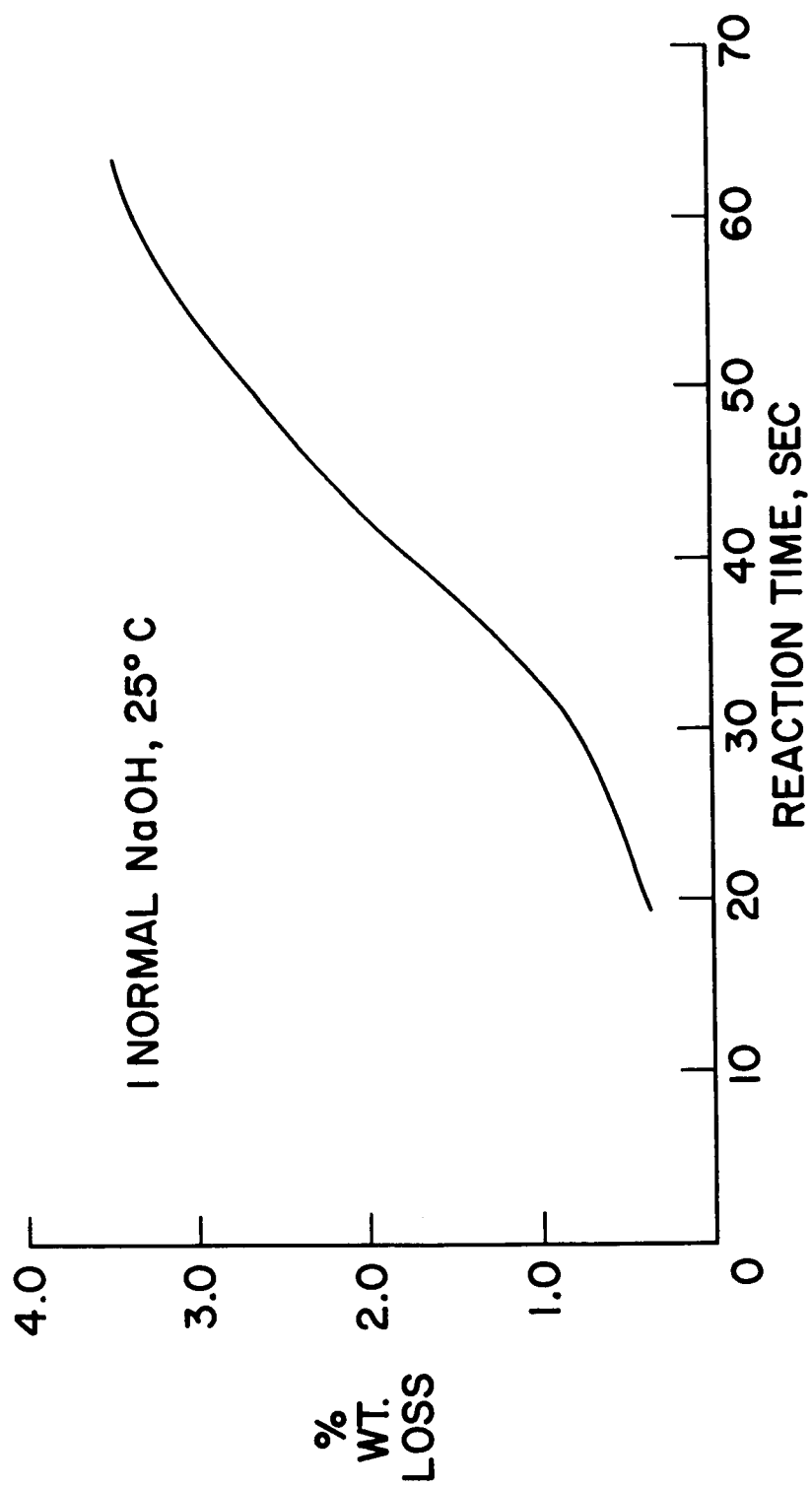
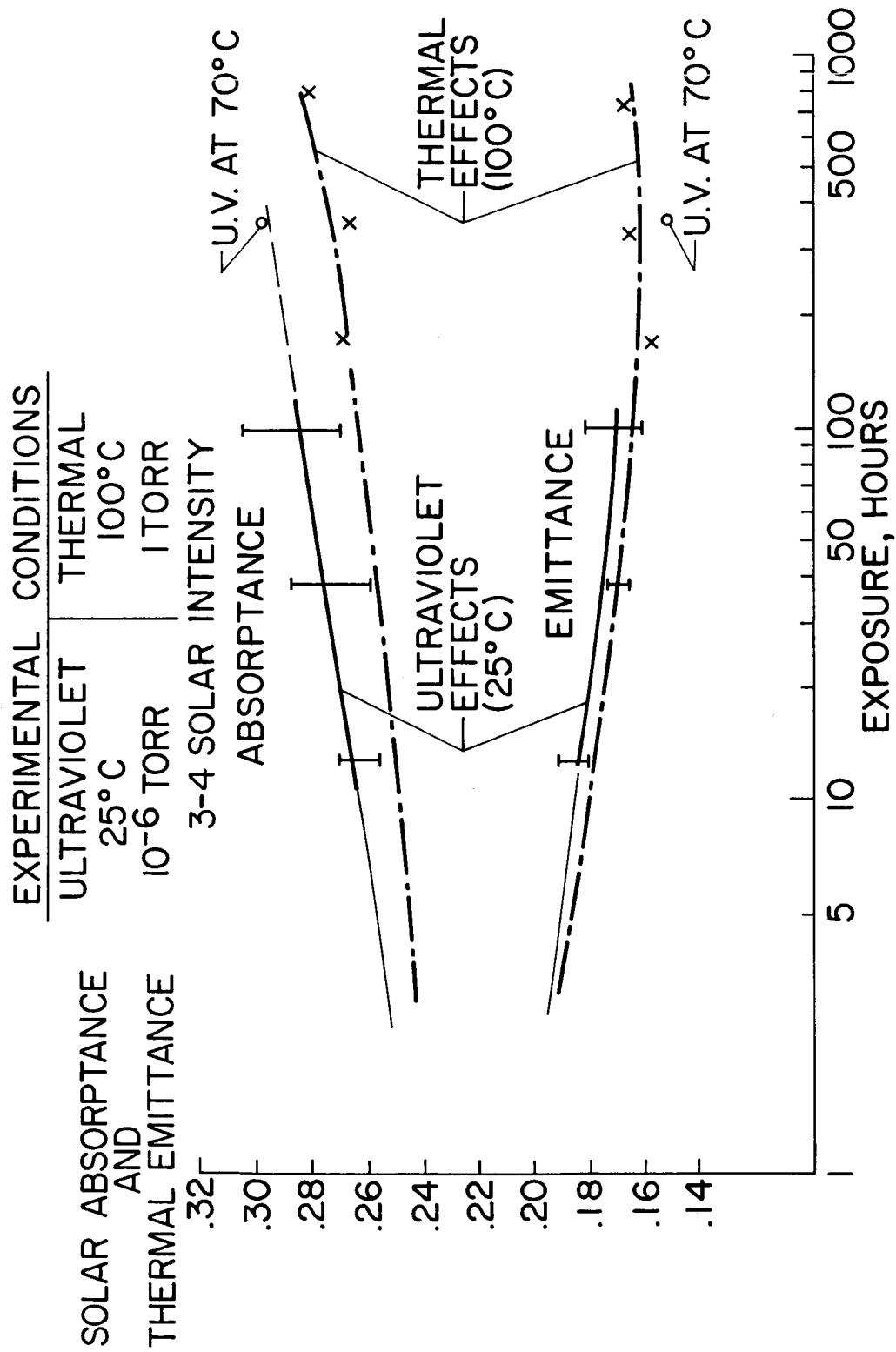


Figure 5.- Effect of reaction time on ratio of absorbance to emittance.



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Figure 6.- Weight loss from reaction with sodium hydroxide.



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Figure 7.- Thermal and ultraviolet effects on solar absorptance and thermal emittance of Alodine 401.

ENVIRONMENTAL CONDITIONS  
 TEMPERATURE 100° C  
 PRESSURE APPROX. 1 TORR.  
 TIME, HOURS:

A - 0  
 B - 168  
 C - 336  
 D - 504

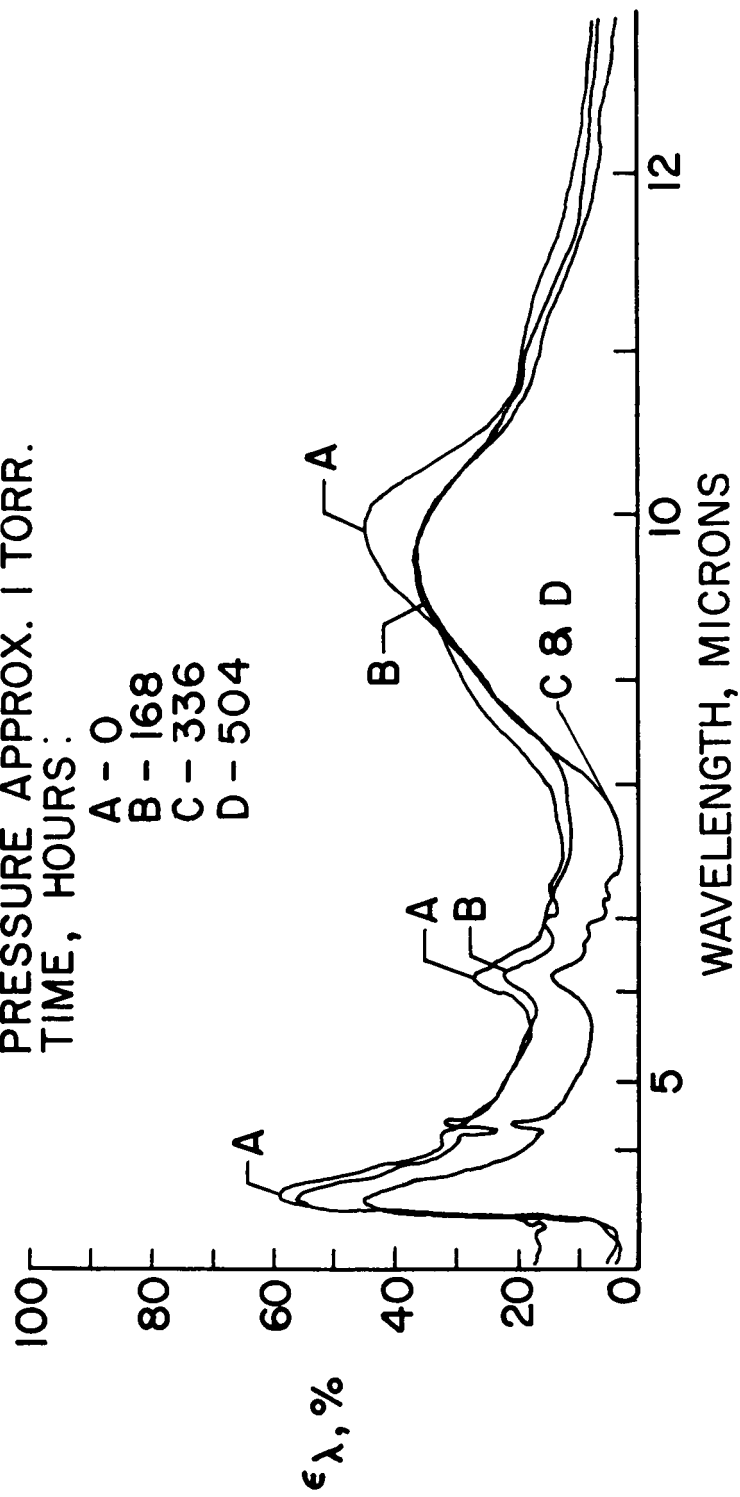
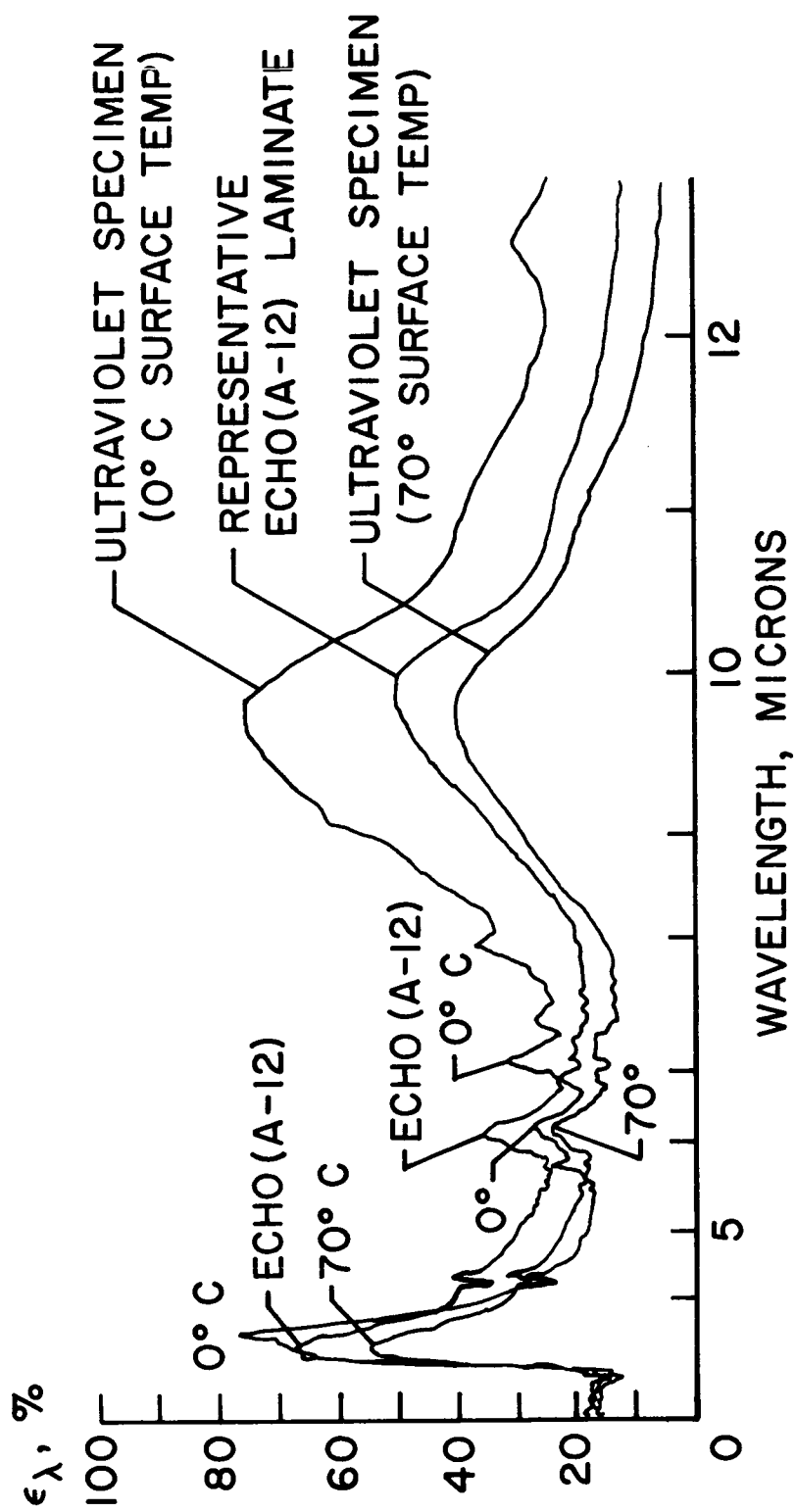


Figure 8.- Thermal effect on the infrared spectra of alodine 401.



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Figure 9.- Effect of ultraviolet degradation at different temperatures on infrared spectra of Alodine 401.

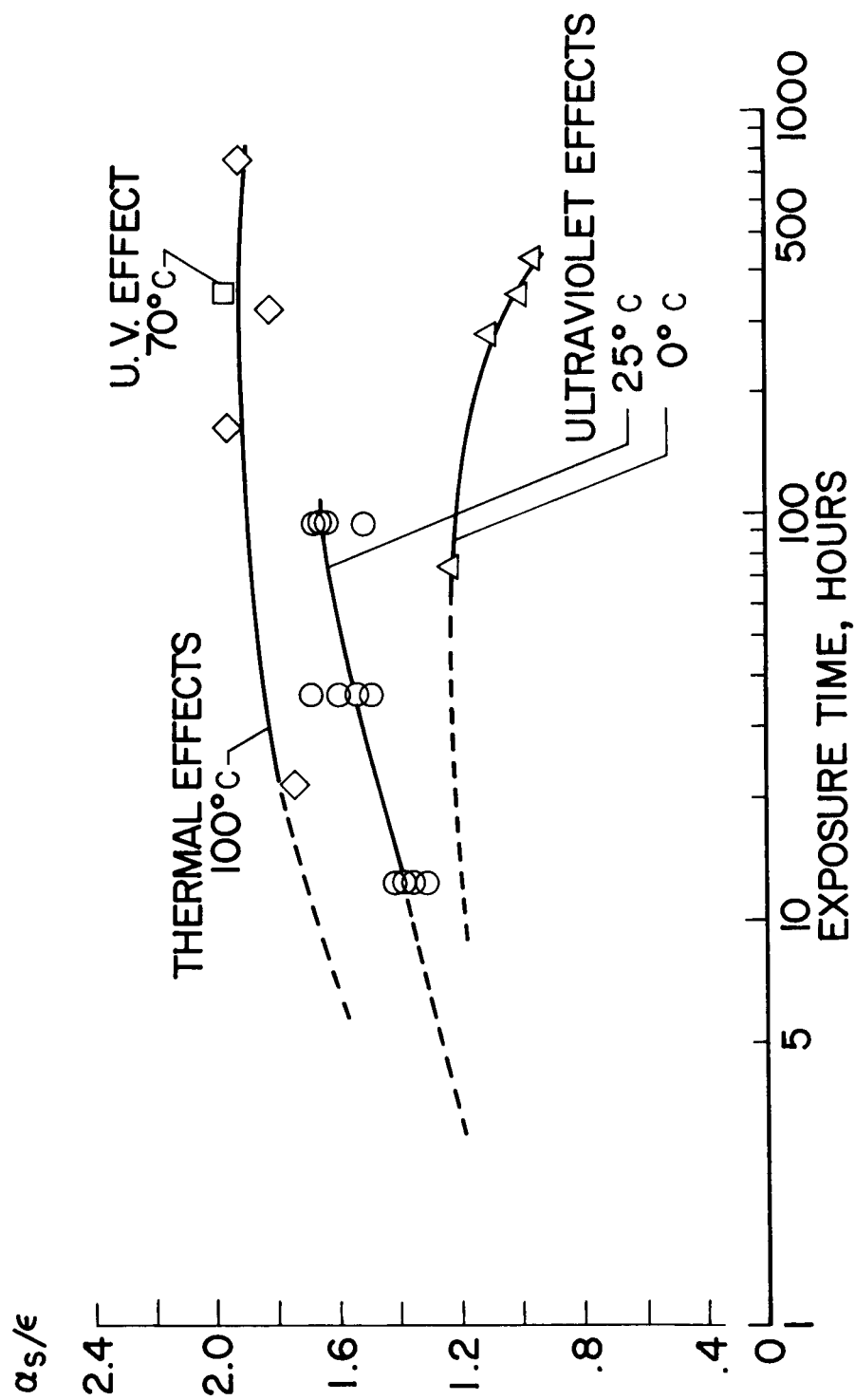
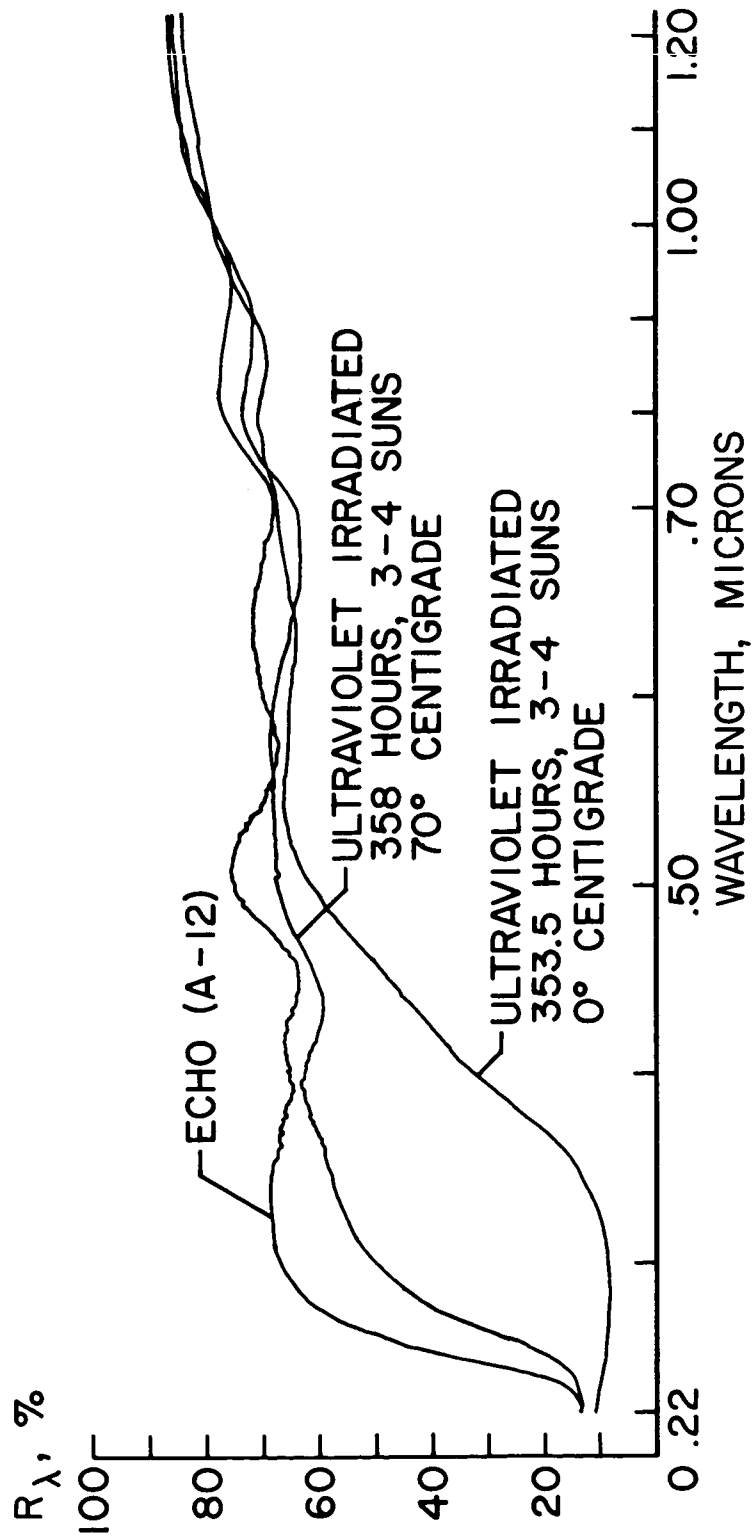


Figure 10.- Comparison of thermal and ultraviolet effects on  $\alpha_s/\epsilon$ .



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Figure 11.- Reflectance spectra for ultraviolet exposure at different temperatures.